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TECHNICAL TRANSLATION 125

ON THE HIGH REACTIVITY OF PEROXIDE
RADICALS IN AN OXIDATION-REDUCTION
REACTION

V. M. GOL'DBERG
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FROM DOKLADY AKADEMII NAUK SSSR 164. 4: 860-863 (1965)



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Translated by U.S. Joint Publications Research Service
from Doklady Akademii Nauk SSSR 164. 4: 860-863 (1965)

Feltman Research Laboratory
Picatinny Arsenal
Dover, N.J.

UDC 542.943.8

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By V. M. Gol'dberg and L. K. Obukhova

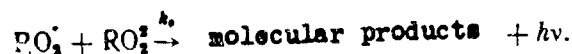
Doklady Akademii Nauk SSSR (Reports of the Academy of Sciences
USSR), 1965, Vol 164, No 4, pp 860-863.

(Presented by Academician V. N. Kondrat'yev on 29 March 1965)

The salts of variable-valence metals are widely used as oxidizing catalysts for various organic substances. It is known that the rate of the oxidation reaction directly depends on the concentration of the active centers -- the peroxide radicals $RO_2\cdot$. Because the peroxide radical displays the properties of an oxidizing agent, under certain conditions it can interact with a metal salt in the state of lower valence. Then the migration of one electron from Me^{n+} to the radical $RO_2\cdot$ results in the destruction of free valence (breaking of the oxidation chain). A macrokinetic consequence of this elementary act is the decrease in oxidation rate [1, 2]. In some cases the presence of a manganese salt in the reaction zone may result in complete cessation of the developing chain process of oxidation [3].

At present, this class of reactions -- the interaction between salts of transition metals and radicals -- has remained virtually uninvestigated from the quantitative standpoint. Our previous investigation [4] showed that the rate constant of the reaction between a complex salt of divalent manganese and the radical $RO_2\cdot$ in the medium of an oxidizing hydrocarbon amounts to 10^5 l/mol·sec. For greater accuracy of quantitative determination, the chemiluminescence method [5] was employed in the present investigation. The interaction between peroxide radicals and manganese stearate was investigated with the aid of a chemiluminescence setup described by Vasil'yev et al. [6].

It is known that hydrocarbon oxidation reactions are accompanied by a glow due to the process of the quadratic recombination of peroxide radicals:



If the peroxide radicals are generated in the reaction at a constant rate w_1 , then $w_1 = k_2[RC_2^{\cdot}]^2 = \text{const}$, and the intensity of chemiluminescence will remain constant. If an agent (inhibitor) reacting with RO_2^{\cdot} is added to such a reacting system, the rate of quadratic recombination will decrease and the intensity of chemiluminescence will correspondingly decrease.

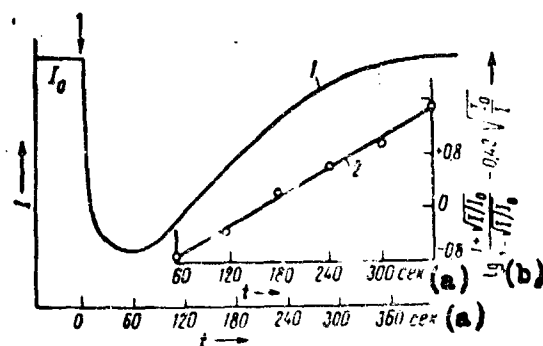


Fig. 1. 1 -- Kinetic curve of variation in glow intensity during interaction between RO_2^{\cdot} and $MnSt_2$ (arrow denotes the instant of addition of a solution of manganese stearate to the reaction); 2 -- Anamorphosis of curve 1 in coordinates of equation (4a).

a -- sec; b -- log.

Fig. 1 shows a typical chemiluminescence diagram. The reaction was carried out in a thermostat-controlled glass reaction vessel with bubbling of oxygen through the solution and in the presence of an activator (dibromoanthracene) in the concentration of 1 mg/ml. The source of the radicals was azobisisobutyronitrile and the inert solvent was chlorobenzene. As can be seen from Fig. 1, the steady-state regime characterizing the decomposition of the initiator in chlorobenzene involves a constant chemiluminescence intensity. Following the addition of manganese stearate (indicated by arrow in figure), the glow intensity rapidly diminishes but later, as the manganese passes into its trivalent form, re-attains its previous value. In this experiment the temperature was $80^{\circ}C$, $[MnSt_2] = 1.3 \cdot 10^{-5}$ mol/l, $w_1 = 5 \cdot 10^{-8}$ mol/l·sec.

Consider the reactions that occur in this system, consisting of the inert solvent, the initiator Y and the transition-metal salt MnSt_2 .

1. $Y \xrightarrow{w_i} \text{RO}_2^\cdot$.
2. $\text{RO}_2^\cdot + \text{RO}_2^\cdot \xrightarrow{k_6} h\nu$ quadratic rupture [of chain of oxidation].
3. $\text{RO}_2^\cdot + \text{MnSt}_2 \xrightarrow{k_7} \text{MnOHSt}_2 + \text{molecular products}$.

The kinetics of these reactions is described by the system of differential equations

$$d[\text{RO}_2^\cdot] / dt = w_i - k_7[\text{RO}_2^\cdot][\text{Mn}] - k_6[\text{RO}_2^\cdot]^2; \quad (1)$$

$$d[\text{Mn}] / dt = -k_7[\text{RO}_2^\cdot][\text{Mn}]. \quad (2)$$

As shown by Karpukhin et al. [7], the concentration of radicals is proportional to the square root of the glow intensity

$$[\text{RO}_2^\cdot] = [\text{RO}_2^\cdot]_0 \sqrt{I/I_0} = \sqrt{w_i/k_6} \sqrt{I/I_0},$$

where $[\text{RO}_2^\cdot]$, I , $[\text{RO}_2^\cdot]_0$ and I_0 are the concentrations of radicals and the intensities of chemiluminescence at the instant of initiation and at the initial instant (i.e., prior to the addition of the manganese salt), respectively. Substituting this relation in (1) and utilizing the steady-state principle, we have

$$\begin{aligned} & \sqrt{w_i/k_6} d(\sqrt{I/I_0})/dt = w_i - k_7 \sqrt{w_i/k_6} \sqrt{I/I_0} [\text{Mn}] - k_6 \frac{w_i}{k_6} \frac{I}{I_0} = 0, \\ & [\text{Mn}] = \frac{w_i - k_6 (w_i/k_6) (I/I_0)}{k_7 \sqrt{w_i/k_6} \sqrt{I/I_0}} = \frac{\sqrt{w_i \cdot k_6}}{k_7} \left(\sqrt{\frac{I_0}{I}} - \sqrt{\frac{I}{I_0}} \right) = \frac{\sqrt{w_i \cdot k_6}}{k_7} \frac{I_0 - I}{\sqrt{I_0 I}}. \end{aligned} \quad (3)$$

We denote $\sqrt{I/I_0} = x$ and substitute the determined values of $[\text{RO}_2^\cdot]$ and $[\text{Mn}]$ in equation (2):

$$dx \left[\frac{1}{x^2(1-x^2)} + \frac{1}{1-x^2} \right] = k_7 \sqrt{\frac{w_i}{k_6}} dt. \quad (4)$$

Integrating this equation, we have

$$\ln \left[\frac{1+x}{1-x} \right] - \frac{1}{x} = k_7 \sqrt{\frac{w_i}{k_6}} t + C. \quad (4a)$$

In the coordinates of this equation, the time dependence of chemiluminescence intensity must be linear and the ratio $k_7/\sqrt{k_6}$ can be derived from the tangent of the angle of slope for a given value of w_i .

In Fig. 1, the straight line 1 represents the time dependence of

$$\log \frac{1 + \sqrt{I/I_0}}{1 - \sqrt{I/I_0}} - 0,43 \sqrt{\frac{I_0}{I}}$$

the value of $k_7/\sqrt{k_6}$ calculated from this plot is 76.0 (l/mol·sec)^{1/2}. The mean value of the ratio $k_7/\sqrt{k_6}$, obtained by a similar method from findings on six experiments, is 75.0 (l/mol·sec)^{1/2}.

The ratio $(I_0 - I)/\sqrt{II_0}$ at any time instant can be computed from the chemiluminescence diagram; according to equation (3), this ratio is proportional to the concentration of MnSt₂. Curve 1 in Fig. 2 describes the time dependence of $(I_0 - I)/\sqrt{II_0}$ i.e., reflects the variation in [Mn] in the course of the reaction. The semilogarithmic anamorphosis of this curve (straight line 2) shows that, beginning with a certain degree of transformation, the change in the concentration of the salt resembles a first-order reaction. This is understandable if it is considered that for a chemiluminescence intensity equal to one-half of the initial intensity the concentration of radicals amounts to 70 percent of the initial quantity [RO₂]₀. As the manganese salt becomes consumed, [RO₂] rises back to its original level. Thus, over the longer interval of the reaction, the concentration of radicals changes 30%, i.e., may to some approximation be considered constant. Then

$$-d[Mn]/dt \cong k_7 [RO_2]_0 [Mn] = k_7 \frac{\sqrt{w_1}}{\sqrt{k_6}} [Mn] \quad (10).$$

The value of $k_7/\sqrt{k_6}$ calculated from the slope of the semilogarithmic anamorphosis is 56.

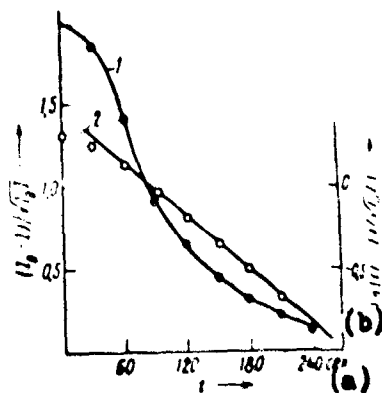


Fig. 2. 1 -- Kinetic curve of variation in the concentration of the manganese salt; 2 -- Semilogarithmic anamorphosis of curve 1.

a -- sec; b -- log.

Lastly, the current concentration of $[Mn]$ can be graphically calculated. In Fig. 1, the area below the curve of chemiluminescence intensity is proportional to the amount of the radicals that underwent mutual recombination, while the area between this curve and the straight-line curve of $I = I_0$ is proportional to the amount of radicals that reacted with Mn^{2+} or, which is the same thing, to the amount of manganese salt that switched to another valence. Fig. 3 presents the quantity $(I_0 - I) / \sqrt{I_0 I}$ as a function of $[Mn]$ as graphically calculated. The linearity is fulfilled satisfactorily; from this plot we have $k_7 / \sqrt{k_6} = 36 \text{ (l/mol} \cdot \text{sec)}^{1/2}$.

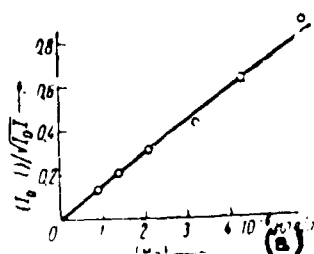


Fig. 3. The Quantity $(I_0 - I) / \sqrt{I_0 I}$ as a Function of $[Mn]$ Calculated Graphically from Curve 1 in Fig. 1.

a -- mol/l.

All the above techniques of analysis of experimental findings make it possible only to determine the relative rate constant of the interaction between RO_2^{\cdot} and $MnSt_2$. The determination of the absolute value of this quantity requires knowledge of the rate constant k_6 of the recombination of radicals RO_2^{\cdot} . The chemiluminescent method makes it possible also to determine this value in the event that the reaction follows an unsteady-state regime [8], i.e., with a rapid change in initiation rate to $(w_1)_2$ from $(w_1)_1$. Integrating the equation

$$d[RO_2^{\cdot}] / dt = w_1 - k_6[RO_2^{\cdot}]^2$$

and substituting the value of $[RO_2^{\cdot}]$ expressed through chemiluminescence intensity, we have

$$\log \frac{1+x}{1-x} - \log \frac{1+x_1}{1-x_1} = \frac{2}{2.3} \sqrt{w_1 k_6} t, \quad (5)$$

where $x = I/I_0$, $x_1 = I_1/I_0$, I_1 and I_0 are the intensities of chemiluminescence in the initial and terminal states of the system, respectively.

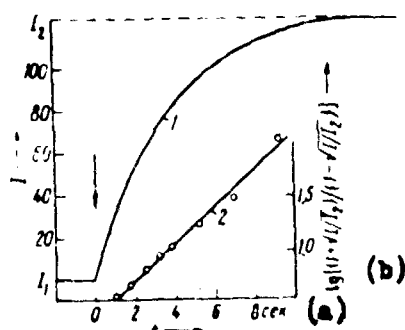


Fig. 4. 1 -- Kinetic curve of variation in chemiluminescence intensity during unsteady regime of reaction; 2 -- Anamorphosis of curve 1 in coordinates of equation (5).

a -- sec; b -- log.

The experiments were performed as follows: a new portion of the solution of azobisisobutyl cyanide was added (Fig. 4, curve 1, time instant of addition indicated by arrow) to the reaction vessels in which the steady-state process of decomposition of the initiator occurred at a given temperature. Glow intensity was observed to change for 5-10 sec, after which a constant chemiluminescence current, corresponding to a new steady state of the reaction, set in again. Control experiments showed that the addition of a quantity of cold solution to the reaction zone as well as the stirring time both do not markedly affect the kinetics of the unsteady-state reaction. In the coordinates of equation (5), the kinetic curve of the unsteady variation in intensity of chemiluminescence becomes transformed to a straight-line curve (Fig. 4, straight line 2). The value of the rate constant of recombination was calculated as the geometric mean of five quantities (Table 1).

Table 1

$k_r \cdot 10^{10} \text{ mol/l} \cdot \text{sec}$	1.35	1.21	1.20	1.06	0.6
$k_r \cdot 10^7 \text{ l/mol} \cdot \text{sec}$	2.25	2.32	1.89	0.85	1.24
					$\text{av} = 1.6$

Assuming that k_r is independent of temperature, these experimental findings make it possible to calculate the absolute rate constant of the reaction between RO_2^\cdot and MnSt_2 (in $\text{l/mol} \cdot \text{sec}$, $^{1/2}$): at 60°C , $k_r = 2.0 \cdot 10^8$; at 70°C , $k_r = 2.4 \cdot 10^8$; at 80°C , $k_r = 3 \cdot 10^8$ or $k_r = 2.8 \cdot 10^8 \exp(-4800 \text{ kcal/RT})$. These values of the preexponent and activation energy are close to the corresponding values for the reaction of interaction between the radicals RO_2^\cdot and strong inhibitors [9]. As is known, the transition potential for $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ is 1.5 ev or 35 kcal. Apparently, the reason for the low activation energy

of the interaction between RO_2 and MnSt_2 is that a heteropolar rather than ionic bond is then formed.

Institute of Chemical Physics
Academy of Sciences USSR

Submitted
25 March 1965

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UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION
Picatinny Arsenal, Dover, New Jersey		Unclassified
		2b. GROUP
3. REPORT TITLE		
ON THE HIGH REACTIVITY OF PEROXIDE RADICALS IN AN OXIDATION-REDUCTION REACTION		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Translated from Doklady Akademii Nauk SSSR 164. 4: 860-863 (1965)		
5. AUTHOR(S) (First name, middle initial, last name)		
V. M. Gol'dberg L. K. Obukhova		
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 1968	7	10
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO.	Technical Translation 125	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT		
[REDACTED] must		
[REDACTED] Jersey.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY
13. ABSTRACT		
<p>The salts of variable-valence metals are widely used as oxidizing catalysts for various organic substances. It is known that the rate of the oxidation reaction directly depends on the concentration of the active centers -- the peroxide radicals $RO_2\cdot$. Because the peroxide radical displays the properties of an oxidizing agent, under certain conditions it can interact with a metal salt in the state of lower valence. Then the migration of one electron from Me^{n+} to the radical $RO_2\cdot$ results in the destruction of free valence (breaking of the oxidation chain). A macrokinetic consequence of this elementary act is the decrease in oxidation rate. In some cases the presence of a manganese salt in the reaction zone may result in complete cessation of the developing chain process of oxidation.</p> <p>At present, this class of reactions -- the interaction between salts of transition metals and radicals -- has remained virtually uninvestigated from the quantitative standpoint. The interaction between peroxide radicals and manganese stearate was investigated with the aid of a chemiluminescence setup described by Vasil'yev et al.</p>		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Peroxide radicals (RO_2^\cdot)						
Hydrocarbon oxidation reaction						
Chemiluminescence						
Inhibitors						
Variable-valence metals						
Oxidizing catalysts						
Oxidation chains						
Azobisisobutyronitrile						
Dibromoanthracene						
Chlorobenzene						
Manganese stearate						
Semilogarithmic anamorphosis						
Techniques for analysis of experimental findings						
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